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Polymer processing aid from rubber seed oil, a renewable resource: Preparation and characterization

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Vulcanized vegetable oil (VVO), a polymer processing aid was prepared from sulphur and rubber seed oil (RSO), a renewable resource. RSO was obtained from the seeds of the rubber tree (*Hevea brasiliensis*) which are in abundance in Nigeria but are unexploited. The effect of additives such as iodine, magnesium oxide (MgO), sodium carbonate (Na_2CO_3), 2-mercaptobenzothioazole (MBT) and zinc diethyldithiocarbonate (ZDEC) on the vulcanization process was investigated. The vulcanized RSO (VRSO) obtained was characterized in terms of hardness, free sulphur, ash content and acetone extract. The results obtained showed that the properties of vulcanized oil produced from RSO are dependent on the additive used.

Key words: Vulcanized vegetable oil, rubber seed oil, additives, Nigeria.

INTRODUCTION

Vulcanized vegetable oil (VVO) has been used in the rubber industry for a long time as a valuable processing aid. It is made by vulcanizing unsaturated vegetable oils. VVO is regarded as a very important rubber compounding ingredient because of certain intrinsic properties which it possesses that are indispensable in mixes during milling, calendering, extrusion and injection moulding (Donnelly, 1963; Flint et al., 1969). VVO gives dimensional stability to extruded articles, reduces mould fill time and cure cycle time, improves the ozone resistance of the rubber compound, gives a smooth velvety feel to rubber articles, reduces migration of plasticizers to the surface of rubber stock and has ability to promote flow under mechanical pressure (Erhan and Kleiman, 1990). It is used during the production of rubber tubing, automobile parts, window seals and cable coverings. Its ability to break easily makes it the major component in eraser formulations.

Physical properties such as colour, hardness, acetone extract and free sulphur values (SV) are used to judge the quality of VVO. Free sulphur is the unreacted or lightly bound sulphur during the vulcanization process. Acetone extract is the amount of unreacted oil and partially sulphurized glyceride oil extractable from the polymer matrix. VVO with acetone extract values less than 20% is regarded as first grade, greater than 20% but less than 35% is medium grade, and greater than 35% as commercial grade (Reynolds, 1962). However, a higher acetone extract value does not necessarily imply that the VVO is inferior for a particular application; VVO is specifiable only by its actual performance in tests in rubber, and not by simple chemical tests alone

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Table 1. Typical composition of long- chain fatty acids in soybean and Linseed oil (Nag et al., 1995) and Rubber seed oil (Aigbodion and Bakare, 2005).

Fatty acid	Linseed oil	Soybean oil	RSO
Saturated acids			
$C_{16:0}$	7	12	11
$C_{18:0}$	5	5	12
$C_{20:0}$	0.1	1.5	1.0
Unsaturated acids			
$C_{18:1}$	24	30	24
$C_{18:2}$	22	58	39
$C_{18:3}$	55	9	24

(Lower, 1984).

Though VVO has been used for several years, only limited number of vegetable oils such as soybean oil, castor oil, rapeseed oil, crambe oil and linseed oil are used in its preparation (Erhan and Kleiman, 1990). Some of these oils, particularly soybean oil are also used for edible purposes. Linseed oil is an imported commodity in Nigeria with the attendant drain on the nation foreign exchange. Rubber seed oil (RSO), which at the moment is not yet recommended as edible and of no economic value in the country, is a potential oil for VVO production. It has over 82% unsaturated fatty acids consisting of oleic acid (17 to 24%), lenoleic acid (35 to 39%) and lenolenic (16 to 24%) (Iyayi et al., 2008). It compares favourably with linseed and soybean oils in the fatty acids composition as shown in Table 1.

The double bonds which are present in the oil can easily be cross linked with sulphur to form VVO. These bonds are also exploited in the production of compounds such as alkyd resin used as binder in surface coating, epoxidized oil used as plasticizer-stabilizer in polymers and various others end products (Iyayi et al., 2007) from the oil.

This study therefore, was carried out with the purpose of exploring the use of RSO in the production of vulcanized oil as well as determining the effect of different additives on the properties of the vulcanized oil.

MATERIALS AND METHODS

Rubber seeds from which the oil was extracted were obtained from the plantation of Rubber Research Institute of Nigeria during the harvest period of August to September. The seeds were dried to a moisture content of about 7% and were thereafter subjected to mechanical extraction process using a hydraulic press. Sulphur (sublimed) (Hopkin and Williams, Essex England) and carbon disulphide was from J. T. Baker USA. Magnesium oxide (MgO), 2-mercaptobenzothiozole (MBT), zinc diethyldithiocarbonate (ZDEC) and sodium carbonate (Na_2CO_3), all of reagent grade were from Aldrich Chemical Co., Wisconsin USA. Iodine (resublimed) was from Lab Tech Chemicals. Acetone analytical grade was from BDH chemicals Ltd Poole England.

In the production of vulcanized RSO (VRSO), 100 ml of the crude RSO (free fatty acid; FFA 37.96%, IV 142.45, SV 226.12) was placed in a 400 ml beaker and heated in an oil bath to the reaction temperature of 160°C. Thereafter, sulphur and other additives (accelerators) were slowly added to the oil, while stirring to prevent sulphur from forming big lumps. The viscosity of the reaction mixture gradually increased, while it was constantly stirred until it started to solidify. The colour of the reaction mixture also changed from light brown at the initial stage to dark towards the final stages. The heating was stopped and the reaction mixture was allowed to cool to room temperature.

The physical properties of VRSO, such as ash content, acetone extract, free sulphur and hardness were determined. For ash analysis, 1 g of the sample in porcelain crucible was ignited in a muffle furnace at a temperature of 850°C for an hour. Thereafter, the mass was withdrawn from the furnace and allowed to cool in a dessicator, weighed repeatedly until constant weight was attained. The weight was used to calculate the ash content. Acetone extract value of the VVO was determined on 1 g of the ground sample which was extracted by acetone repeatedly in Soxhlet extractor for 2 h. Thereafter, the residual mass was dried to constant weight. The difference between the initial and final weight was the mass of the extracted materials which was then used to determine the percentage soluble materials in acetone. In the determination of free sulphur, 1 g of the ground sample was extracted repeatedly by carbon disulphide in a Soxhlet extractor for 1 h. Thereafter, the sample was withdrawn and dried at room temperature. The free sulphur was the difference in weight between the initial weight of the sample and that after the extraction. Hardness tests were done with hand-held Durometer Hardness Tester.

RESULTS AND DISCUSSION

Table 2 shows the physical properties of VRSO prepared with different proportions of sulphur. When 30 parts per hundred parts of oil (pho) was used, gelling of the oil began slowly after 14 min. This did not produce any solid mass even after a reaction time of 1 h. It produced a sticky, soft and dark coloured product which on cooling formed a semi-solid mass. The same trend was observed for lower proportions of sulphur (15 to 25 pho) though at different gel times. This time, they produced only sticky and soft products after cooling the reaction mass. These results indicate that the quantity of sulphur used affected the gelling time and the physical properties of the

Table 2. Physical properties of VRSO at 160°C.

Oil	Sulphur (pho)	Gel time (min)	Hardness (IRHD)[a]	Acetone extract (%)	Free sulphur (%)	Ash (%)
Crude oil	30	14	NA[b]	30.88	5.28	0.88
	25	23	NA[b]	43.70	4.60	0.76
	20	28	NA[b]	83.16	3.40	0.69
	15	35	NA[b]	83.32	3.14	0.85

[a]International rubber hardness degree. [b]Not applicable, sample too soft to be measured; pho = Parts per hundred parts of oil.

Table 3. Effect of additives on the physical properties of VRSO using crude RSO.

S/N	Additive (pho)[a]	Sulphur (pho)	Gel time (min)	Hardness (IRHO)	Acetone Extract (%)	Free Sulphur (%)	Ash (%)
1	MgO (10)	30	6	74	14.98	3.41	5.80
	MgO (10)	25	7	65	18.39	2.68	6.07
	MgO (10)	20	7	62	30.85	2.60	5.79
	MgO (10)	15	8	50	62.30	2.58	6.56
2	Na_2CO_3 (10)	30	7	48	21.85	4.11	7.49
	Na_2CO_3 (10)	25	8	45	17.63	3.32	7.33
	Na_2CO_3	20	10	NA[b]	27.12	3.25	6.10
	Na_2CO_3 (10)	15	33	NA[b]	24.09	3.08	7.39
3	MBT (4)	30	No gel	NA[c]	50.81	4.21	1.12
	ZDEC (4)	30	No gel	NA[c]	45.79	3.60	1.42
	Iodine (0.3)	30	No gel	NA[c]	45.70	2.33	1.05

[a] Parts per hundred parts of oil; [b] Not applicable, sample was solid but not hard enough to be measured; [c] Not applicable, sample too soft to be measured; MBT = Mercaptobenzothiozole; ZDEC = Zinc diethyldithiocarbonate.

vulcanized oil. Sticky vulcanized oil is not very desirable in that it presents difficulties during manufacturing and transportation as well as cleaning difficulty in the reactor (Erhan and Kleiman, 1990). Acetone extract and free sulphur content were affected by variation in the quantity of sulphur used. The higher the quantity of sulphur used, the lower the acetone extract and the higher the free sulphur content. Ash content was higher for 30 pho but there was no significant difference in ash content for lower SV. The dark colour of VVO is reported be a measure of the iodine value (IV) (Carrington, 1962). The higher the IV of the vegetable oil used, the darker is the vulcanized oil. The IV of RSO, 142.45 is considered high, hence, the observed dark colour of the VRSO.

Furthermore, some accelerators (additives) were used to determine their effect on the vulcanization process. Erhan and Kleiman (1990) have demonstrated that many accelerators and polymerization initiators that are used in the vulcanization reactions of rubber could also be used for vegetable oil vulcanization. Accelerators, as reported by Stem (1967), increase the rate of sulphur combination by breaking down the stable form of sulphur into sulphides and polysulphides which then release sulphur in active form. They also increase efficiency and utilization of sulphur as a cross linking agent and produce a simpler network. Of the accelerators (additives) used in this study, MgO and Na_2CO_3 (Table 3) gave shorter gelling time, hard products and low free sulphur compared with the experiments without accelerators. This agrees with earlier investigation (Carrington, 1962) that the use of such accelerators led to harder VVO, lower free sulphur and shortens the time of gelling in some cases by a factor of two. However, the other accelerators such as MBT, ZDEC and iodine, did not form any gel but produced soft sticky dark mass when the reaction products were cooled. However, the use of all accelerators led to the improvement in acetone extract but the ash content was higher for MgO and Na_2CO_3 than for the other accelerators. In all, MgO seemed to have produced better results than the rest of the accelerators.

The effect of the quantity of accelerator, MgO blended with other additives such as MBT, ZDEC and iodine on the physical properties of the VRSO was also determined. As the quantity of MgO was reduced

Table 4. Effect of quantity and blends of additives on the physical properties of VRSO using crude RSO.

Additive (pho)[a]	Sulphur (pho)[a]	Gel time (min)	Hardness (IRHD)	Acetone extract (%)	Free sulphur (%)	Ash (%)
MgO (10)	25	6	74	14.98	2.68	5.80
MgO (8)	25	8	74	15.05	2.68	4.66
MgO (6)	25	10	59	15.58	2.60	5.39
MgO (4)	25	10	45	19.16	2.72	4.58
MBT/MgO (10)	25	13	32	23.51	3.24	5.52
ZDEC/MgO (10)	25	10	75	14.14	3.30	6.54
Iodine(0.3)/MgO (10)	25	15	65	20.99	2.10	8.05

[a]Parts per hundred parts of oil.

(Table 4), gel time increased and the acetone extract also increased but the hardness of the VRSO was reduced progressively. Although there was a change in the free sulphur as the quantity of MgO was reduced, it was not significant. A blend of MgO with the accelerators such as MBT, ZDEC and iodine showed remarkable improvement in the physical properties of the VRSO produced compared to when these accelerators were used alone even when the amount of sulphur used was high (Table 3).

Conclusions

From this study, the following conclusions can be drawn:

1. That VVO can be produced from RSO and sulphur. Without additive, sticky and soft products are obtained with high gel time. With higher sulphur loading, the gel time is reduced and less sticky products are obtained.
2. The use of additives (accelerators) such as MgO and Na_2CO_3 with crude oil are effective in giving shorter gel times and products with enhanced physical properties. MgO is much better in producing harder products which are desirable as this eases handling difficulties, while MBT, ZDEC and iodine are not effective accelerators when acting alone. A blend of MgO with them is found to improve their effectiveness.

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